

# PATENT SPECIFICATION

(11) 1268419

1268419

## NO DRAWINGS

(21) Application No. 42048/69 (22) Filed 22 Aug. 1969  
 (31) Convention Application No. 59925 (32) Filed 23 Aug. 1968  
 (31) Convention Application No. 2622 (32) Filed 16 Jan. 1969  
 (31) Convention Application No. 5728 (32) Filed 28 Jan. 1969  
 (31) Convention Application No. 53763 (32) Filed 9 July 1969 in  
 (33) Japan (JA)  
 (45) Complete Specification published 29 March 1972  
 (51) International Classification C 08 c 11/44  
 (52) Index of acceptance  
 C3Q C16B C16C C17 C18B C20A C20B C20C C20D1  
 C7 C8B D1A T2A  
 C3P 2C16B 2C16C 2C17 2C18 2C20A 2C20B 2C20C  
 2C20D1 2C7 2C8B 2H6 2HY 2R2



## (54) RUBBER COMPOSITIONS CONTAINING ANTIOZONANTS

(71) We, SHOWA DENKO KABUSHIKI KAISHA, a Japanese Body Corporate, of No 34, Shiba Miyamoto-cho, Minato-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a rubbery polymer composition containing antiozonants which prevent degradation of natural and synthetic rubbers by ozone, and which are non-discolouring and non-staining.

Natural and synthetic rubbers are generally degraded under the influence of oxygen, heat, light and particularly ozone. Even the trace of ozone present in the air causes cracks on the surfaces of rubber articles exposed thereto for a prolonged period. The degrading and cracking action of ozone is particularly accelerated when the rubber article is under stress. The recent increase in the discharge of exhaust gas from automobiles and the rapid development of the petrochemical industries are causing a remarkable increase in the ozone concentration in the air. Thus the problem of degradation of rubber articles by ozone is becoming all the more serious.

Various antiozonants for rubber have been previously proposed, for example urea or thiourea derivatives (U.S. Patent Specifications Nos. 2,766,219; 2,781,330; 2,788,338 and British Patent Specification No. 887,174), aliphatic amine derivatives (U.S. Patent Specification No. 3,436,368) and aromatic amine derivatives. However, all known antiozonants are subject to one defect or another. Thiourea derivatives (e.g. N,N' - di butylthiourea, N,N' - dicyclohexylthiourea or the N,N' - dialkylalkylenediamines) are non-

discolouring and non-staining, but exhibit insufficient antiozonant action. On the other hand, aromatic amine derivatives [e.g. N-phenyl - N - isopropyl - p - phenylenediamine and N,N' - di - (2 - naphthyl) - p - phenylenediamine], show a practical level of antiozonant activity, but they discolour disagreeably rubber articles with the passage of time, when the rubber articles are exposed to light. Some of those known antiozonants are themselves coloured compounds, and therefore they can be used only with dark coloured rubbers, for example those containing carbon black. Furthermore, discolouration of rubber is caused by such known amine type antiozonants because they migrate to the surface and then into the adjacent areas of the rubber article. For example, with an automobile tyre, the discolouration of the dark coloured rubber layer containing such an antiozonant gradually migrates into the side wall layer of white rubber adhered to the former layer, to discolour disagreeably the surface of the white rubber layer. This migratory property is normally referred to as the "staining property" in this art.

It has now been discovered that N-substituted derivatives of xylylenediamine and xylylenediamines having one or two alkyl ring substituents are excellent antiozonants for rubber, and thus very effectively prevent the degradation of rubber caused by ozone. Furthermore, these compounds are themselves colourless or white, have no colouring action on rubber, show no discolouration under exposure to light, and have no staining property. The antiozonants used in the invention are different from the known aliphatic or aromatic amine type antiozonants in that the former are of the aralkylene diamine type, i.e. the nitrogen atoms of the two amino

[Price 25p]

45

50

55

60

65

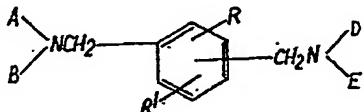
70

75

80

radicals are each linked with the benzene ring through a methylene radical. It is presumed that the two active methylene radicals linked with the two nitrogen atoms contribute to the excellent properties of the compounds as the antiozonants.

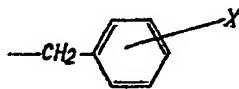
The invention therefore provides a composition comprising a sulphur-vulcanisable rubbery polymer and 0.1 to 5 parts by weight, per 100 parts by weight of the rubbery polymer, of a compound of the general formula (I)



wherein each of R and R', which may be the same or different, is a hydrogen atom or a lower alkyl group, and each of A, B, D and E, which may be the same or different, is a hydrogen atom; an alkyl, cycloalkyl, aryl or aralkyl group of up to 20 carbon atoms; a group of the formula  $-\text{CH}_2\text{Y}$ , Y being a 5- or 6-membered heterocyclic residue containing in all 1 or 2 atoms of oxygen, sulphur and/or nitrogen; or a group of the formula  $-(\text{CHR}^2)_n\text{Z}$ , R<sup>2</sup> being a hydrogen atom or a methyl group, n being 1 or 2, and Z being a hydroxy, cyano or carboxyl group; not more than two of A, B, D and E being hydrogen atoms. The compound can be used in the form of a salt or ester.

The terms "lower alkyl" and "lower alkoxy" as used herein refer to those groups having 1 to 4 carbon atoms.

An example of a suitable aryl group is a (lower alkoxy) phenyl group, while suitably the aralkyl group is a group of general formula



wherein X is a halogen atom or a hydroxy, lower alkyl, lower alkoxy, (lower alkyl)amino or di(lower alkyl)amino group.

The derivatives of the *m*- or especially *p*-xylylenediamines are preferred. Mixtures of the meta- and para-derivatives can be used with equal effect. Furthermore, the compounds in which at least one of A, B, D and E is a benzyl or substituted benzyl group exhibit a most excellent antiozonant effect.

The compounds of general formula (I) can be readily prepared by conventional synthetic means, for example by dehydrohalogenating a haloalkane with a xylylenediamine, by reducing Schiff's base obtained by condensation of a carbonyl compound with a xylylenediamine, or by reacting an unsaturated compound con-

taining a polar radical (e.g. acrylonitrile) with xylylenediamine.

The compounds can be applied broadly to natural and various synthetic rubbers, for example, butadiene rubber, styrene - butadiene rubber, acrylonitrile - butadiene rubber, isoprene rubber, isobutylene - isoprene rubber and chloroprene rubber. Since they do not cause discolouration nor do they possess the staining property, they can be very advantageously applied to white or light-coloured rubber articles.

The amount of the compound is preferably 0.5-3 parts by weight per 100 parts of the rubbery polymer. The compounds can be blended into the rubbery polymer during the vulcanisation thereof. The compounds have no detrimental effect on the other rubber additives, for example sulphur (used as vulcanising agent), vulcanising accelerators (e.g. dibenzothiazyl disulphides), vulcanising activators (e.g. zinc oxide and stearic acid) and fillers (e.g. calcium carbonate, titanium oxide and silica).

The invention is illustrated by the following Recipes:

Various compounds of general formula (I) were blended with natural and synthetic rubbers. The rubber samples employed were white rubber compositions prepared by milling the compositions recipe below on a roll-mill, and vulcanising at 140° C. for 20 minutes. The rubbers were natural rubber (NR-RSS No. 1) and synthetic styrene - butadiene rubber (SBR No. 1502). Controls containing no antiozonant, or containing conventional antiozonants, for example N-phenyl - N'-isopropyl - *p* - xylylenediamine, N,N'-dibutyl-thiourea, and N,N' - di(2 - naphthyl) - *p*-xylylenediamine were also investigated.

Recipe:	Parts (by weight):	95
Rubber component .....	100	
Calcium carbonate .....	100	
Stearic acid .....	1	
Zinc oxide .....	5	
Sulphur .....	2.5	100
Dibenzothiazyl disulphide ...	1	
Antiozonant .....	2	

The following tests were performed:

(A) Crack occurrence test due to degradation caused by ozone:

The sample (150×25×2 mm.) was held at 38° C. in an atmosphere containing 50 parts per hundred million of ozone, under stretching to 20% elongation, and the time (in hours) which passed before cracks detectable to the eye through a magnifying lens was measured. The results are shown in the Table.

(B) Discolouration and staining test:

A layer of the sample containing the antiozonant was pressed against a layer of sample

containing no antiozonant, at 100° C. for 4 hours. The multi-layered samples were left outside for three days, and the discolouration in the antiozonant-containing rubber and the migration of the discolouration to the antiozonant-free rubber layer were observed. To facilitate the observation, the antiozonant-free rubber was prepared from a white rubber composition formed of the components listed in the above Recipe plus 20 parts by weight of titanium oxide but with no anti-ozonant. The staining property was evaluated in the four classes below, according to the degree of staining of the antiozonant-free rubber.

15      Class 0: No staining  
       Class 1: Slight staining  
       Class 2: Considerable staining  
       Class 3: Heavy staining

All of the rubber compositions containing the compounds of general formula (I) and the one containing N,N' - dibutylthiourea did not show any discolouration under exposure to sunlight, and consequently the staining property was in these cases in class 0. In clear contrast thereto, the control samples containing N - phenyl - N' - isopropyl - p - phenylenediamine and N,N' - di(2 - naphthyl - p - phenylenediamine were both discoloured to yellowish brown after approximately 20 hours, and the staining property was in class 3 for the former, and class 2 for the latter.

The Table below gives the specific antiozonant employed in each run, and the results for the crack occurrence test. The symbol, "m,p" refers to a mixture of the meta and para derivatives in a ratio of 7:3 by weight.

TABLE

Sample No.	Antiozonant used	Time passed before cracks were formed (hr.)	
		NR-RSS#1	SBR#1502
a	(Control) none	3	1
b	(Control) N-phenyl-N'-isopropyl-p-phenylenediamine	8	7.5
c	(Control) N,N'-dibutylthiourea	6	4
d	(Control) N,N'-di(2-naphthyl)-p-phenylenediamine	5	3
1	N-benzyl-N'-ethyl-p-xylylenediamine	24	20
2	N-benzyl-N'-cyclohexyl-m,p-xylylenediamine	21	21
3	N-benzyl-N'-phenyl-p-xylylenediamine	25	26
4	N-benzyl-N'-isopropyl-2,5-dimethyl-p-xylylenediamine	20	20
5	N,N'-dibenzyl-m-xylylenediamine	24	26
6	N,N'-dibenzyl-m,p-xylylenediamine	30	29
7	N,N'-dibenzyl-2,5-dimethyl-1,4-xylylenediamine	28	28
8	N,N'-bis(4-ethylbenzyl)-m-xylylenediamine	20	23
9	N,N'-bis(4-t-butylbenzyl)-p-xylylenediamine	31	32
10	N,N'-diisopropyl-m-xylylenediamine	11	10
11	N-isobutyl-N'-cyclohexyl-m,p-xylylenediamine	12	10
12	N,N'-dicyclohexyl-m-xylylenediamine	13	13
13	N-isopropyl-N'-phenyl-m,p-xylylenediamine	15	15
14	N,N'-diphenyl-p-xylylenediamine	15	14

TABLE (Continued)

15	N-isopropyl-N'-( <i>p</i> -methoxyphenyl)- <i>p</i> -xylylenediamine	15	15
16	N-isopropyl-N'-phenyl-2,5-dimethyl-1,4-xylylenediamine	13	12
17	N,N'-di(1-naphthyl)- <i>p</i> -xylylenediamine	27	23
18	N,N'-di(2-naphthyl)- <i>p</i> -xylylenediamine	26	23
19	N,N'-di(1-naphthylmethyl)- <i>p</i> -xylylenediamine	30	25
20	N,N'-diphenethyl- <i>p</i> -xylylenediamine	22	19
21	N- <i>m</i> -methylbenzyl-N'-isopropyl- <i>m,p</i> -xylylenediamine	21	22
22	N,N'-bis(2-naphthylmethyl)- <i>p</i> -xylylenediamine	29	25
23	N,N'-dimethyl-N-benzyl- <i>p</i> -xylylenediamine	21	22
24	N,N-dibenzyl-N'-isopropyl- <i>m,p</i> -xylylenediamine	25	21
25	N,N,N'-tribenzyl- <i>m</i> -xylylenediamine	30	26
26	N,N,N'-tribenzyl-2,5-dimethyl- <i>p</i> -xylylenediamine	25	23
27	N-phenyl-N-methyl-N'-benzyl xylylenediamine	23	23
28	N,N'-dicyclohexyl-N-phenyl- <i>m,p</i> -xylylenediamine	15	15
29	N-lauryl-N,N'-dimethyl- <i>p</i> -xylylenediamine	13	12
30	N,N'-bis( <i>p</i> -chlorobenzyl)- <i>p</i> -xylylenediamine	32	30
31	N,N'-bis( <i>p</i> -methoxybenzyl)- <i>m,p</i> -xylylenediamine	23	23
32	N,N'-bis( <i>p</i> -methylaminobenzyl)- <i>m</i> -xylylenediamine	26	25
33	N- <i>p</i> -chlorobenzyl-N'-isopropyl- <i>p</i> -xylylenediamine	29	26
34	N- <i>p</i> -hydroxybenzyl-N'-ethyl- <i>m,p</i> -xylylenediamine	28	25
35	N- <i>p</i> -hydroxybenzyl-N'-benzyl- <i>p</i> -xylylenediamine	30	28
36	N,N,N'-tris( <i>p</i> -chlorobenzyl)- <i>m,p</i> -xylylenediamine	32	30
37	N,N'-bis( <i>p</i> -hydroxybenzyl)-N-benzyl- <i>p</i> -xylylenediamine	30	29
38	N,N,N',N'-tetramethyl- <i>m</i> -xylylenediamine	15	13
39	N,N'-dimethyl-N,N'-dibenzyl- <i>m,p</i> -xylylenediamine	20	21
40	N,N'-dimethyl-N,N'-diisopropyl- <i>p</i> -xylylenediamine	19	20
41	N,N'-dimethyl-N,N'-dicyclohexyl- <i>m,p</i> -xylylenediamine	16	18
42	N,N,N',N'-tetrabenzyl- <i>m</i> -xylylenediamine	25	27
43	N,N,N',N'-tetrabenzyl-2,5-dimethyl-1,4-xylylenediamine	25	26
44	N,N,N',N'-tetrakis( <i>p</i> -chlorobenzyl)- <i>m,p</i> -xylylenediamine	25	23

TABLE (Continued)

45	N,N'-bis( <i>p</i> -chlorobenzyl)-N,N'-dibenzyl- <i>m,p</i> -xylylenediamine	21	19
46	N,N,N'-tris( <i>m</i> -dimethylaminobenzyl)-N'-benzyl- <i>p</i> -xylylenediamine	25	23
47	N,N'-bis(2-furylmethyl)- <i>p</i> -xylylenediamine	21	20
48	N,N'-bis(2-thienylmethyl)- <i>m,p</i> -xylylenediamine	19	19
49	N,N'-bis(2-pyridylmethyl)- <i>m,p</i> -xylylenediamine	24	22
50	N,N'-bis(2-furylmethyl)-N,N'-bis( $\beta$ -hydroxyethyl)- <i>m,p</i> -xylylenediamine	21	20
51	N,N'-bis( $\beta$ -cyanoethyl)2,5-dimethyl- <i>p</i> -xylylenediamine	21	20
52	N,N'-bis(ethoxycarbonylmethyl)- <i>m,p</i> -xylylenediamine	21	17
53	N,N'-bis(ethoxycarbonylethyl)- <i>m</i> -xylylenediamine	23	22
54	N,N,N',N'-tetrakis( $\beta$ -cyanoethyl)- <i>m,p</i> -xylylenediamine	27	26
55	N,N,N',N'-tetrakis(butoxycarbonylmethyl)- <i>p</i> -xylylenediamine	18	18
56	N,N,N',N'-tetrakis(ethoxycarbonylethyl)- <i>m,p</i> -xylylenediamine	19	17
57	N,N,N',N'- <i>p</i> -Xylylenediamine-tetraacetic acid	23	21
58	N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-dibenzyl- <i>p</i> -xylylenediamine	30	26

## WHAT WE CLAIM IS:—

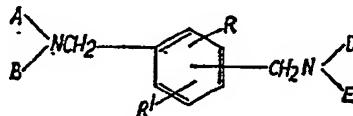
1. A composition comprising a sulphur-vulcanisable rubbery polymer and 0.1 to 5 parts by weight, per 100 parts by weight, of the rubbery polymer of a compound of the general formula (I)

Z being a hydroxy, cyano or carboxyl group; not more than two of A, B, D and E being hydrogen atoms.

2. A composition according to claim 1 wherein the compound of general formula (I) is in the form of a salt or ester.

3. A composition according to claim 1 or 2 wherein the aryl group is a (lower alkoxy)-phenyl group.

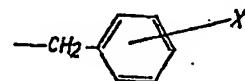
4. A composition according to claim 1 wherein the aralkyl group has the general formula

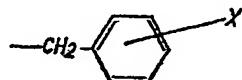


10 wherein each of R and R', which may be the same or different, is a hydrogen atom or lower alkyl group, and each of A, B, D and E, which may be the same or different, is a hydrogen atom; an alkyl, cycloalkyl, aryl or aralkyl group of up to 20 carbon atoms; a group of the formula  $-\text{CH}_2\text{Y}$ , Y being a 5- or 6-membered heterocyclic residue containing in all 1 or 2 atoms of oxygen, sulphur and/or nitrogen; or a group of the formula  $-(\text{CHR}^2)^n\text{Z}$ , R<sup>2</sup> being a hydrogen atom or a methyl group, n being 1 or 2, and

15 wherein X is a halogen atom or a hydroxy, lower alkyl, lower alkoxy, (lower alkyl)amino or di(lower alkyl)amino group.

20 A composition according to claim 1 wherein R and R' are hydrogen atoms or lower alkyl groups, A and D are hydrogen atoms, and B and E are benzyl groups or groups of general formula





wherein X is a lower alkyl group.

6. A composition according to claim 1 wherein A, B, D and E are alkyl, cycloalkyl, aryl or aralkyl groups having 1 to 10 carbon

5 atoms, and the group  $\text{---CH}_2\text{N}^{\text{D}}\text{---}$  is in the para- or meta-position.

10 7. A composition according to claim 1 wherein R and R' are hydrogen atoms or lower alkyl groups, A and D are hydrogen atoms and B and E are alkyl, cycloalkyl or aryl groups.

15 8. A composition according to claim 1, wherein the compound of general formula (I) is N,N' - dibenzyl - m- or p - xylylenediamine.

19 9. A composition according to claim 1, wherein the compound of general formula (I) is N,N' - bis(4 - t - butylbenzyl) - p - xylylenediamine.

20 10. A composition according to claim 1, wherein the compound of general formula (I) is N,N' - di(1 - naphthylmethyl) - p - xylylenediamine.

25 11. A composition according to claim 1, wherein the compound of general formula (I) is N,N' - bis(p - chlorobenzyl) - p - xylylenediamine.

30 12. A composition according to claim 1, wherein the compound of general formula (I) is N,N,N' - tribenzyl - m - xylylenediamine.

13. A composition according to claim 1 wherein the compound of general formula (I) is N,N,N' - tribenzyl - p - xylylenediamine.

14. A composition according to claim 1, 35 wherein the compound of general formula (I) is N,N,N',N' - tetrakis(p - chlorobenzyl) - m- or p - xylylenediamine.

15. A composition according to claim 1, 40 substantially as hereinbefore described in the foregoing Recipes.

16. A process for the production of a vulcanised rubbery article which comprises shaping and sulphur-vulcanising a composition according to any one of claims 3, 4, 9, 10, 13 45 and 15.

17. A process for the production of a vulcanised rubbery article which comprises shaping and sulphur-vulcanising a composition according to any one of claims 1, 2, 11, 12 50 and 14.

18. A process for the production of a vulcanised rubbery article which comprises shaping and sulphur-vulcanising a composition according to claim 7.

19. A process for the production of a vulcanised rubbery article which comprises shaping and sulphur-vulcanising a composition according to claim 6.

20. A process for the production of a vulcanised rubbery article which comprises shaping and sulphur-vulcanising a composition according to claim 5 or 8.

21. Vulcanised rubber articles obtained by a process according to claim 16.

22. Vulcanised rubber articles obtained by a process according to claim 17.

23. Vulcanised rubber articles obtained by a process according to claim 18.

24. Vulcanised rubber articles obtained by a process according to claim 19.

25. Vulcanised rubber articles obtained by a process according to claim 20.

J. A. KEMP & CO.,  
Chartered Patent Agents,  
14, South Square, Gray's Inn,  
London, WC1R 5EU.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.